

Pure rotation spectrum of CF₄ in the $\nu_3 = 1$ state using THz synchrotron radiation



V. Boudon^{a,*}, M. Carlos^{a,b,c}, C. Richard^a, O. Pirali^{d,e}

^a Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS – Université Bourgogne Franche-Comté, 9 Av. A. Savary, BP 47870, F-21078 Dijon Cedex, France

^b Université de Toulouse, UPS-OMP, Institut de Recherche en Astrophysique et Planétologie, Toulouse, France

^c CNRS, IRAP, 9 Av. Colonel Roche, BP 44346, F-31028 Toulouse Cedex 4, France

^d Ligne AILES-Synchrotron SOLEIL, L'Orme des Merisiers, F-91192 Gif-sur-Yvette Cedex, France

^e Institut des Sciences Moléculaires d'Orsay (ISMO), CNRS, Univ. Paris-Sud, Université Paris-Saclay, F-91405 Orsay, France

ARTICLE INFO

Article history:

Received 27 June 2017

In revised form 12 July 2017

Accepted 12 July 2017

Available online 14 July 2017

Keywords:

Carbon tetrafluoride
Synchrotron radiation
Pure rotation
Non-polar molecule
Dipole moment

ABSTRACT

Spherical-top tetrahedral species like CH₄, SiH₄, CF₄, ... possess no permanent dipole moment. Therefore, probing their pure rotation spectrum is very challenging since only a very weak dipole moment can be induced by centrifugal distortion and/or rovibrational interaction. If some Q branch lines have been recorded thanks to microwave techniques, R branch lines in the THz region have been poorly explored until recently. In previous studies, we have reported the pure rotation THz spectrum of cold and hot band lines of methane recorded at the SOLEIL Synchrotron facility. Here, we present the first recorded THz spectrum of the R branch of CF₄, a powerful greenhouse gas, in its $\nu_3 = 1$ state. This Fourier transform spectrum covers the R(20) to R(37) line clusters, in the 20–37 cm^{−1} spectral range. It was recorded thanks to a 150 m multiple path cell at room temperature. We could estimate the vibration-induced dipole moment value and also include the recorded line positions in a global fit of many CF₄ transitions.

© 2017 Elsevier Inc. All rights reserved.

1. Introduction

Tetrafluoromethane (CF₄), is a strong infrared absorber in the 7.8 μm spectral region [1]. This, combined with its chemical inertness and industrial uses [2] makes it a powerful greenhouse gas of anthropogenic origin with a huge lifetime in the Earth's atmosphere [3,4]. The *in situ* detection of atmospheric CF₄ is based on infrared absorption spectroscopy [5–9]. The public spectroscopic databases like HITRAN [10,11] or GEISA [12,13], however, are not complete enough for atmospheric applications, because of an incomplete spectroscopic characterization of this molecule [1].

We recently performed a global analysis of many rovibrational bands of this molecule, in order to obtain a reliable simulation of CF₄'s atmospheric absorption, including hot bands [14]. In the case of such non-polar molecules with no permanent dipole moment, it appears difficult to observe pure rotation lines. Such data are, however, complementary to infrared rovibrational lines to help for a precise determination of effective Hamiltonian parameters, especially for the ground vibrational state. In previous works, we could observe and accurately measure line positions, line intensities and

line broadening coefficients for the methane (CH₄) molecule's pure rotation spectrum [15,16].

In the present paper, written as a complement to Ref. [14], we report the very first observation of rotational lines of CF₄. This molecule is heavier than CH₄ and thus rotational lines lie at lower wavenumbers, due to smaller inertia constants. At present, we could only observe $\nu_3 - \nu_3$ lines, *i.e.* pure rotational transitions within the $\nu_3 = 1$ vibrational state. These lines appear to be very weak and observing them in the 20–37 cm^{−1} region required a long optical path, a relatively high gas pressure and the use of synchrotron radiation in order to obtain a reasonable signal-to-noise ratio.

Section 2 reports the experimental details. Section 3 recalls some basic principles concerning the theory of such a rotational spectrum. Section 4 presents our results, including a rough estimate of the corresponding dipole moment derivative parameter.

2. Experimental details

The pure rotation spectrum within the $\nu_3 = 1$ vibrational state of CF₄ has been recorded in the 20–40 cm^{−1} spectral range using the Fourier Transform interferometer installed on the SOLEIL AILES beamline. The synchrotron operation mode was a 500 mA total current multibunch mode. We used a 1.7 K cooled bolometer and

* Corresponding author.

E-mail address: vincent.boudon@u-bourgogne.fr (V. Boudon).

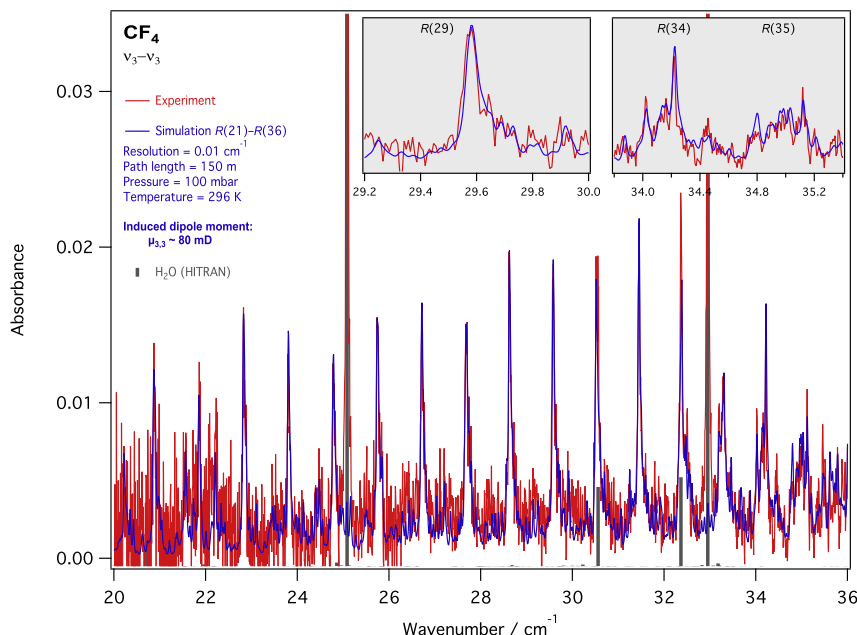


Fig. 1. Measured $v_3 - v_3$ lines in the R branch, compared to the simulation. Grey ticks show water lines taken from the HITRAN database [24]. The inserts detail three line clusters.

a 6 μm thick mylar beamsplitter. The absorption cell was a room-temperature multipass cell adjusted to reach 151.75 ± 1.5 m absorption pathlength. The CF₄ pressure was set to 99.6 ± 0.1 mbar and 5040 spectra were coadded. The reference spectra were obtained by filling the cell with about 100 mbar of He to prevent baseline variations due to mechanical constraints in the cell; 2880 reference scans were coadded. Since CF₄ lines were pressure broadened, all spectra were recorded at a 0.01 cm^{-1} spectral resolution.

3. Theoretical model

To model the spectrum, we use the theoretical model based on the tensorial formalism developed by the Dijon group [17,18]. It takes full advantage of the molecule's high symmetry. The basic principles of this approach, applied to CF₄, have been recalled in our recent paper about the global analysis of this molecule [14]. We use here the same effective Hamiltonian as in this paper, in order to calculate the energy levels. It should be noticed that the global fit of Ref. [14] includes line positions from the present study.

In the present paper, however, we report on line intensities, so we give here some details about the effective dipole moment operator.

As a spherical top, CF₄ has no permanent dipole moment. But, when applying to the full dipole moment operator of the molecule the same contact transformation as the one used to isolate the different rovibrational polyads (see [19] for more details), some induced dipole moment terms appear even for pure rotational transitions. We consider here the effective dipole moment operator for $v_3 - v_3$ transitions,

$$\mu_{\{v_3-v_3\}}^{(\mu_3-\mu_3)} = \mu_{\{\text{GS-GS}\}}^{(\mu_3-\mu_3)} + \mu_{\{v_3-v_3\}}^{(\mu_3-\mu_3)} = \mu_0 R^{2(2,F_2)} + \mu_{3,3} V_{3,3}^{F_2 F_2(F_2)} + \dots \quad (1)$$

As explained in [19,17], the effective dipole moment for hot bands is based on an extrapolation scheme. The $v_3 - v_3$ effective dipole moment contains two terms in the right member of Eq.

(1). The first one is $\mu_{\{\text{GS-GS}\}}^{(\mu_3-\mu_3)}$ and corresponds to a centrifugal distortion-induced dipole moment in the Ground State (GS). $R^{2(2,F_2)}$ is a rotational operator [19]. This term should be very small and the value of its μ_0 parameter is not known, since no pure rotational line in the ground state have been observed yet, contrary to the CH₄ case [15].

The second term in the right member of Eq. (1) is the dipole moment derivative that is specific to $v_3 - v_3$ transitions. $V_{3,3}^{F_2 F_2(F_2)}$ is a vibrational operator relative to these transitions (see [19] for details about the tensorial construction of vibrational operators for tetrahedral molecules), while $\mu_{3,3}$ is the corresponding parameter to be determined. This one is related to the $(\mu_z)_{\text{eff}}$ parameter of Mills *et al.* [20] through the relation [21]

$$\mu_{3,3} = -\sqrt{6} (\mu_z)_{\text{eff}}. \quad (2)$$

4. Dipole moment derivative determination

We performed a spectrum simulation using the XTDS software [22] and using the effective Hamiltonian from Ref. [14]. Using the same temperature, pressure and path length conditions as for the experiment (see Section 2), we then tuned manually the $\mu_{3,3}$ parameter value in order to let the simulation match the experimental spectrum. Due to spectrum congestion and to the high pressure, it is not possible here to measure individual components of the pure rotational lines within the $v_3 = 1$ vibrational state.

Although the experimental spectrum has a relatively low signal-to-noise ratio, 18 line clusters from $J = 20$ to 37 can be observed. We find a correct match for:

$$\mu_{3,3} \simeq 80 \text{ mD}. \quad (3)$$

The corresponding value in the case of CH₄ is 49 mD [23]. Fig. 1 shows the resulting comparison between experiment and simulation, with a nice agreement.

Table 1

Assigned $v_3 - v_3$ lines included in the global CF₄ fit of Ref. [14]. J is the rotational quantum number, C the rovibrational symmetry (T_d point group irreducible representation) and α a ranking index, while $''$ and $'$ denote lower and upper state values, respectively (all rotational levels pertaining to the $v_3 = 1$ vibrational level, in the present case).

Wavenumber/cm ⁻¹	J''	C''	α''	J'	C'	α'
20.873032	20	A_1	12	21	A_2	16
20.873032	20	A_2	11	21	A_1	14
20.873032	20	F_1	32	21	F_2	45
20.873032	20	F_2	33	21	F_1	45
20.892634	20	A_1	13	21	A_2	17
21.863562	21	A_2	12	22	A_1	17
22.204885	32	A_1	18	33	A_2	21
22.825124	33	A_1	17	34	A_2	21
22.825124	33	A_2	19	34	A_1	23
22.825124	33	E	35	34	E	42
22.825124	33	F_1	53	34	F_2	63
22.825124	33	F_2	54	34	F_1	62
23.802564	23	A_2	14	24	A_1	18
24.778777	24	A_1	15	25	A_2	19
25.740409	25	A_2	15	26	A_1	19
27.682699	27	A_2	16	28	A_1	21
29.581692	29	A_1	16	30	A_2	21
30.514492	30	A_1	18	31	A_2	22
31.454270	31	A_2	18	32	A_1	23
32.378789	32	A_1	19	33	A_2	24
33.188717	33	A_2	20	34	A_1	25
33.304167	33	F_2	53	34	F_1	69
34.020245	34	A_1	21	35	A_2	25
34.219064	34	A_1	19	35	A_2	24
34.219064	34	A_2	19	35	A_1	24
35.119576	35	F_1	57	36	F_2	74
36.875340	37	A_1	19	38	A_2	26

5. Discussion and conclusion

We could observe for the first time pure rotational lines (in the $v_3 = 1$ vibrational state) of a relatively heavy spherical top molecule and we could perform a rough evaluation of the corresponding dipole moment derivative. It is estimated to 80 mD. The line positions from the present study are given in Table 1 and were also used for the global effective Hamiltonian fit described in Ref. [14].

Moreover, we have previously setup a database named TFMe-CaSDa (*Tetra-Fluoro-Methane Calculated Spectroscopic Database*) of the calculated CF₄ spectroscopic lines in the framework of the *Virtual Atomic and Molecular Data Centre* (VAMDC) [25–27]. This one has also been updated, with inclusion of the calculated $v_3 - v_3$ lines using the parameters from the present study to compute line positions and absolute absorption intensities. It is accessible through the VAMDC portal (<http://portal.vamdc.org>) or through the Dat@OSU portal (<https://dataosu.obs-besancon.fr/coll/4>).

A next step would be to observe pure rotational lines in the ground state of CF₄. But these lie at even lower wavenumber and could be very weak (although the μ_0 parameter value is not known). This would thus require a very sensitive technique in the 20–30 cm⁻¹ region, since the present spectra seem too noisy to observe such lines. Maybe the coherent synchrotron radiation [28] or terahertz photomixing [29] could be of help in this case.

References

- [1] E. Mahieu, R. Zander, G.C.T.M.K. Vollmer, S. Reimann, J. Mühle, W. Bader, B. Bovy, B. Lejeune, C. Servais, P. Demoulin, G. Roland, P.F. Bernath, C.D. Boone, K. A. Walker, P. Duchatelet, Spectrometric monitoring of atmospheric carbon tetrafluoride (CF₄) above the Jungfraujoch station since 1989: evidence of continued increase but at a slowing rate, *Atmos. Meas. Tech.* 7 (2014) 333–344.
- [2] M.A.K. Khalil, R.A. Rasmussen, J.A. Culbertson, J.M. Prins, E.P. Grimsrud, M.J. Shearer, Atmospheric perfluorocarbons, *Environ. Sci. Technol.* 37 (2003) 4358–4361.
- [3] A.R. Ravishankara, S. Solomon, A.A. Turnipseed, R.F. Warren, Atmospheric lifetimes of long-lived halogenated species, *Science* 259 (1993) 194–199.
- [4] R.A. Morris, T.M. Miller, A.A. Viggiano, J.F. Paulson, S. Solomon, G. Reid, Effects of electron and ion reactions on atmospheric lifetimes of fully fluorinated compounds, *J. Geophys. Res.* D 100 (1995) 1287–1294.
- [5] A. Goldman, D.G. Murcray, F.J. Murcray, G.R. Cook, J.W.V. Allen, F.S. Bonomo, R. D. Blatherwick, Identification of the v_3 vibration-rotation band of CF₄ in balloon-borne infrared solar spectra, *Geophys. Res. Lett.* 6 (1979) 609–612.
- [6] C.P. Rinsland, E. Mathieu, R. Zander, R. Nassar, P. Bernath, C. Boone, L.S. Chiou, Long-term stratospheric carbon tetrafluoride (CF₄) increase inferred from 1985–2004 infrared space-based solar occultation measurements, *Geophys. Res. Lett.* 33 (2006) L02808.
- [7] R. Zander, M.R. Gunson, C.B. Fanner, C.P. Rinsland, F.W. Irion, E. Mahieu, The 1985 chlorine and fluorine inventories in the stratosphere based on ATMOS observations at 30 north latitude, *J. Atmos. Chem.* 15 (1992) 171–186.
- [8] R. Zander, S. Solomon, E. Mahieu, A. Goldman, C. Rinsland, M.R. Gunson, M.C. Abrams, A.Y. Chang, R.J. Salawitch, H.A. Michelsen, M.J.N. MJ, G.P. Stiller, Increase of stratospheric carbon tetrafluoride (CF₄) based on atmospheric observations from space, *Geophys. Res. Lett.* 23 (1996) 2353–2356.
- [9] B. Sen, G.C. Toon, J.-F. Blavier, E.L. Fleming, C.H. Jackman, Balloon-borne observations of mid-latitude fluorine abundance, *J. Geophys. Res.* 101 (1996) 9045–9054.
- [10] L.S. Rothman, I.E. Gordon, Y. Babikov, A. Barbe, D.C. Benner, P.E. Bernath, M. Birk, L. Bizzocchi, V. Boudon, L.R. Brown, A. Campargue, K. Chance, E.A. Cohen, L.H. Coudert, V.M. Devi, S. Fally, B.J. Drouin, A. Fayt, J.M. Flaud, R.R. Gamache, J. J. Harrison, H.J.-M., C. Hill, J.T. Hodges, D. Jacquemart, A. Jolly, J. Lamouroux, R. Le Roy, G. Li, D.A. Long, O.M. Lyulin, C.J. Mackie, S.T. Massie, S. Mikhailenko, H. Müller, O.V. Naumenko, A.V. Nikitin, J. Orphal, V. Perevalov, A. Perrin, E.R. Polovtseva, C. Richard, M.A.H. Smith, E. Starikova, K. Sung, S. Tashkun, J. Tennyson, G.C. Toon, V.G. Tyuterev, G. Wagner, The HITRAN 2012 molecular spectroscopic database, *J. Quant. Spectrosc. Radiat. Transf.* 130 (2013) 4–50.
- [11] I.E. Gordon, L.S. Rothman, C. Hill, R.V. Kochanova, Y. Tan, P.F. Bernath, M. Birk, V. Boudon, A. Campargue, K.V. Chance, B.J. Drouin, J.-M. Flaud, R.R. Gamache, J. T. Hodges, D. Jacquemart, V.I. Perevalov, A. Perrin, K.P. Shine, M.-A.H. Smith, J. Tennyson, G.C. Toon, H. Tran, V.G. Tyuterev, A. Barbe, A. Csaszar, M.V. Devi, T. Furtenbacher, J.J. Harrison, A. Jolly, T. Johnson, T. Karman, I. Kleiner, A.A. Kyuberis, J. Loos, O.M. Lyulin, S.T. Massie, S.N. Mikhailenko, N. Moazzen-Ahmadi, H.S.P. Müller, O.V. Naumenko, A.V. Nikitin, O.L. Polyansky, M. Rey, M. Rotger, S. Sharpe, K. Sung, E. Starikova, S.A. Tashkun, J.V. Auwera, G. Wagner, J. Wilzewski, P. Wcisło, S. Yu, E.J. Zak, The HITRAN2016 molecular spectroscopic database, *J. Quant. Spectrosc. Radiat. Transf.*, in press, <https://dx.doi.org/10.1016/j.jqsrt.2017.06.038>.
- [12] N. Jacquinet-Husson, L. Crepeau, R. Armante, C. Boutammine, A. Chédin, N.A. Scott, C. Crevoisier, V. Capelle, C. Boone, N. Poulet-Crovisier, A. Barbe, A. Campargue, D.C. Benner, Y. Benilan, B. Bézard, V. Boudon, L.R. Brown, L. Coudert, A. Coustenis, V. Dana, V.M. Devi, S. Fally, A. Fayt, J.-M. Flaud, A. Goldman, M. Herman, G.J. Harris, D. Jacquemart, A. Jolly, I. Kleiner, A. Kleinböhl, F. Kwabia-Tchana, N. Lavrentieva, N. Lacome, L.-H. Xu, O. Lyulin, J.-Y. Mandin, A. Maki, S. Mikhailenko, C.E. Miller, T. Mishina, N. Moazzen-Ahmadi, H.S.P. Müller, A. Nikitin, J. Orphal, V. Perevalov, A. Perrin, D.T. Petkie, A. Predoi-Cross, C.P. Rinsland, J.J. Remedios, M. Rotger, M. Smith, K. Sung, S.

- Tashkun, J. Tennyson, R.A. Toth, A.-C. Vandaele, J.V. Auwera, The 2009 edition of the GEISA spectroscopic database, *J. Quant. Spectrosc. Radiat. Transf.* 112 (2010) 2395–2445.
- [13] N. Jacquinet-Husson, R. Armante, N.A. Scott, A. Chedin, L. Crepeau, C. Boutammine, A. Bouhdaoui, C. Crevoisier, V. Capelle, C. Boonne, N. Poulet-Crovisier, A. Barbe, D.C. Benner, V. Boudon, L.R. Brown, J. Buldyreva, A. Campargue, L.H. Coudert, V.M. Devi, M.J. Down, B.J. Drouin, A. Fayt, C. Fittschen, J.M. Flaud, R.R. Gamache, J.J. Harrison, C. Hill, O. Hodnebrog, S.M. Hu, D. Jacquemart, A. Jolly, E. Jimenez, N.N. Lavrentieva, A.W. Liu, L. Lodi, O.M. Lyulin, S.T. Massie, S. Mikhailenko, H.S.P. Mueller, O.V. Naumenko, A. Nikitin, C. J. Nielsen, J. Orphal, V.I. Perevalov, A. Perrin, E. Polovtseva, A. Predoi-Cross, M. Rotger, A.A. Ruth, S.S. Yu, K. Sung, S.A. Tashkun, J. Tennyson, V.I.G. Tyuterev, J.V. Auwera, B.A. Voronin, A. Makie, The 2015 edition of the GEISA spectroscopic database, *J. Mol. Spectrosc.* 327 (2016) 31–72.
- [14] M. Carlos, O. Gruson, C. Richard, V. Boudon, M. Rotger, X. Thomas, C. Maul, C. Sydow, A. Domanskaya, R. Georges, P. Souillard, O. Pirali, M. Goubet, P. Asselin, T.R. Huet, High-resolution spectroscopy and global analysis of CF_4 rovibrational bands to model its atmospheric absorption, *J. Quant. Spectrosc. Radiat. Transf.* 201 (2017) 75–93.
- [15] V. Boudon, O. Pirali, P. Roy, J.-B. Brubach, L. Manceron, J. Vander Auwera, The high-resolution far-infrared spectrum of methane at the SOLEIL synchrotron, *J. Quant. Spectrosc. Radiat. Transf.* 111 (2010) 1117–1129.
- [16] M. Sanzharov, J.V. Auwera, O. Pirali, P. Roy, J.-B. Brubach, L. Manceron, T. Gabard, V. Boudon, Self and N_2 collisional broadening of far-infrared methane lines measured at the SOLEIL Synchrotron, *J. Quant. Spectrosc. Radiat. Transf.* 113 (2012) 1874–1886.
- [17] V. Boudon, J.-P. Champion, T. Gabard, M. Loëte, F. Michelot, G. Pierre, M. Rotger, C. Wenger, M. Rey, Symmetry-adapted tensorial formalism to model rovibrational and rovibronic spectra of molecules pertaining to various point groups, *J. Mol. Spectrosc.* 228 (2004) 620–634.
- [18] V. Boudon, J.-P. Champion, T. Gabard, M. Loëte, M.R.C. Wenger, Spherical top theory and molecular spectra, in: M. Quack, F. Merkt (Eds.), *Handbook of High-Resolution Spectroscopy*, vol. 3, Wiley, Chichester, West Sussex, United Kingdom, 2011, pp. 1437–1460.
- [19] J.-P. Champion, M. Loëte, G. Pierre, Spherical top spectra, in: K.N. Rao, A. Weber (Eds.), *Spectroscopy of the Earth's Atmosphere and Interstellar Medium*, Academic Press, San Diego, 1992, pp. 339–422.
- [20] I.M. Mills, J.K.G. Watson, W.L. Smith, Rotational spectra induced by vibrations, *Mol. Phys.* 16 (1969) 329–344.
- [21] H. Prinz, W. Höhe, W.A. Kreiner, M. Loëte, J.-C. Hilico, G. Pierre, G. Magerl, W. Schupita, The vibration-induced dipole moment in the ν_2/ν_4 dyad of $^{13}\text{CD}_4$ and $^{28}\text{SiH}_4$, *J. Mol. Spectrosc.* 135 (1989) 144–160.
- [22] C. Wenger, V. Boudon, M. Rotger, M. Sanzharov, J.-P. Champion, XTDS and SPVIEW: graphical tools for the analysis and simulation of high-resolution molecular spectra, *J. Mol. Spectrosc.* 251 (2008) 102–113.
- [23] A. Nikitin, V. Boudon, J.-P. Champion, M. Loëte, S. Albert, S. Bauerecker, M. Quack, L.R. Brown, Global frequency and infrared intensity analysis of $^{12}\text{CH}_4$ lines in the 0–4800 cm^{-1} region, *J. Mol. Spectrosc.* 99 (2007) (999–999).
- [24] L.S. Rothman, I.E. Gordon, A. Barbe, D.C. Benner, P.E. Bernath, M. Birk, V. Boudon, L.R. Brown, A. Campargue, J.P. Champion, K. Chance, L.H. Coudert, V. Dana, V.M. Devi, S. Fally, J.M. Flaud, R.R. Gamache, A. Goldman, D. Jacquemart, I. Kleiner, N. Lacome, W.J. Lafferty, J.Y. Mandin, S.T. Massie, S.N. Mikhailenko, C. E. Miller, N. Moazzen-Ahmadi, O.V. Naumenko, A.V. Nikitin, J. Orphal, V.I. Perevalov, A. Perrin, A. Predoi-Cross, C.P. Rinsland, M. Rotger, M. Simeckova, M. A.H. Smith, K. Sung, S.A. Tashkun, J. Tennyson, R.A. Toth, A.C. Vandaele, J. Vander Auwera, The HITRAN 2008 molecular spectroscopic database, *J. Quant. Spectrosc. Radiat. Transf.* 110 (2009) 533–572.
- [25] M.L. Dubernet, V. Boudon, J.L. Culhane, M.S. Dimitrijevic, A.Z. Fazliev, C. Joblin, F. Kupka, G. Leto, P.L. Sidaner, P.A. Loboda, H.E. Mason, N.J. Mason, C. Mendoza, G. Mulas, T.J. Millar, L.A. Nuñez, V.I. Perevalov, N. Piskunov, Y. Ralchenko, G. Rixon, L.S. Rothman, E. Roueff, T.A. Ryabchikova, A. Ryabtsev, S. Sahal-Bréchet, B. Schmitt, S. Schlemmer, J. Tennyson, V.G. Tyuterev, N.A. Walton, V. Wakelam, C.J. Zeppen, Virtual atomic and molecular data centre, *J. Quant. Spectrosc. Radiat. Transf.* 111 (2010) 2151–2159.
- [26] M.L. Dubernet, B.K. Antony, Y.A. Ba, Y.L. Babikov, K. Bartschat, V. Boudon, B.J. Braams, H.-K. Chung, F. Daniel, F. Delahaye, G.D. Zanna, J. de Urquijo, A. Domaracka, M. Doronin, B.J. Drouin, M.S. Dimitrijevic, C.P. Endres, E. Quintas-Sanchez, A.Z. Fazliev, S.V. Gagarin, I.E. Gordon, U. Heiter, C. Hill, D. Jevremovic, C. Joblin, A. Kasprzak, E. Krishnakumar, G. Leto, P.A. Loboda, T. Lounge, S. Maclot, B.P. Marinkovic, A. Markwick, T. Marquart, H.E. Mason, N.J. Mason, C. Mendoza, A.A. Mihajlov, T.J. Millar, N. Moreau, G. Mulas, G. Leto, Y. Pakhomov, P. Palmeri, S. Pancheshnyi, V.I. Perevalov, N. Piskunov, J. Postler, P. Gratier, P. Quinet, G. Rixon, Y. Ralchenko, Y.-J. Rhee, L.S. Rothman, E. Roueff, T. Ryabchikova, S. Sahal-Bréchet, P. Scheier, S. Schlemmer, B. Schmitt, E. Stempels, J. Tennyson, V. G. Tyuterev, V. Vujcic, V. Wakelam, N.A. Walton, O. Zatsarinny, C.J. Zeppen, C. M. Zwolfthe VAMDC Consortium, The Virtual Atomic and Molecular Data Centre (VAMDC) consortium for astrophysics, *J. Phys. B* 49 (2016) (074003–1–074003–1).
- [27] Y.A. Ba, C. Wenger, R. Surleau, V. Boudon, M. Rotger, L. Daumont, D.A. Bonhommeau, V.G. Tyuterev, M.-L. Dubernet, MeCaSDa and ECaSDa: methane and ethene calculated spectroscopic databases for the virtual atomic and molecular data centre, *J. Quant. Spectrosc. Radiat. Transf.* 130 (2013) 62–68.
- [28] S. Tamaro, O. Pirali, P. Roy, J.-F. Lampin, G. Ducournau, A. Cuisset, F. Hindle, G. Mouret, High density terahertz frequency comb produced by coherent synchrotron radiation, *Nat. Comm.* 6 (2015) 7733.
- [29] G. Mouret, F. Hindle, A. Cuisset, C. Yang, R. Bocquet, M. Lours, D. Rovera, Thz photomixing synthesizer based on a fiber frequency comb, *Opt. Exp.* 17 (2009) 22031–22040.